

Electrochemical Behaviour of Aluminium in Ethyleneglycol-Water Mixtures

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INTRODUCTION

Small dimension-high voltage capacitors have been increasingly demanded by the electronic industry. Among other characteristics, the aluminium capacitors present high reliability and low cost. The anode of the capacitor is a high purity aluminium foil recovered by a Al_2O_3 layer while the cathode is an electrolyte solution. Misfunction in the performance of these devices, such as gas formation and faradaic currents indicates that electrochemical processes dependent on the electrolyte composition may occur.^{1,2} The aim of this study is to investigate the role of the electrolyte composition on the electrochemical behaviour of aluminium in ethyleneglycol-water mixtures, particularly concerning redox reactions occurring in the Al_2O_3 dielectric layer on the metal surface.

EXPERIMENTAL

The electrolytes were analytical grade ethyleneglycol (EG) from Merck, used as received, and ethyleneglycol-water aerated non-buffered solutions containing from 20% to 80% v/v EG and water, in the presence of 0.1 M L^{-1} sodium borate. A disc Al electrode (purity grade 99.99 %, from Goodfellow) was used as working electrode in a conventional 3 electrodes assembly with a saturated calomel reference (SCE) and a Pt gauze auxiliary electrode. Potential measurements are referred to the SCE.

RESULTS AND DISCUSSION

Potentiodynamic voltammetric experiments between -2.0 V and 2.0 V were carried out at the aluminium electrode in EG containing dissolved oxygen. It was observed that faradaic currents appearing above 0.25 V decrease when the electrode is precleaned in $\text{NaOH } 0.1 \text{ M}$ instead of $\text{HCl } 0.1 \text{ M}$, and that no significant difference is observed in the shape of the voltammograms. Consequently, for all experiments the precleaning procedure is carried out in the latter solution.

Open circuit potential (OCP)measurements of the Al disc electrode immersed in EG and water solutions are in the metal passive potential range. On increasing the immersion time the measured OCP shifts toward more positive values, independently of the electrolyte composition, reaching after 60 minutes a potential close to -0.6 V .

Cyclic voltammograms of the Al disc electrode run between $E_{\text{sc}} = -2.0 \text{ V}$ to $E_{\text{sa}} = 5.0 \text{ V}$ at 0.02 V s^{-1} in these solutions are shown in figure 1.

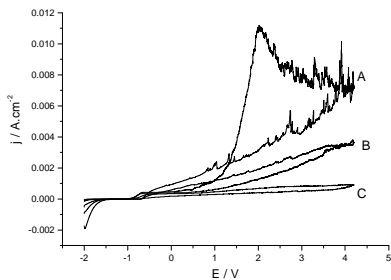


Figure 1. Cyclic voltammograms for the Al disc electrode in solutions containing 20% EG (A), 50% EG (B), 80% EG (C) and water and 0.1 M L^{-1} sodium borate.

It is observed that, with increasing water content, the Al_2O_3 film breakdown takes place while in the pure EG solution the passive film is stable.

Measurements by EIS for the Al disc electrode at the OCP in Bode coordinates, after 5 minutes of immersion in aerated solutions containing from 20% to 80% water and 0.1 M L^{-1} sodium borate are shown in Figure 2. As the EG concentration is increased, the phase angle decreases and the polarization resistance

increases. Furthermore, a diffusional control is observed at lower frequencies, this feature being more pronounced in water rich solutions.

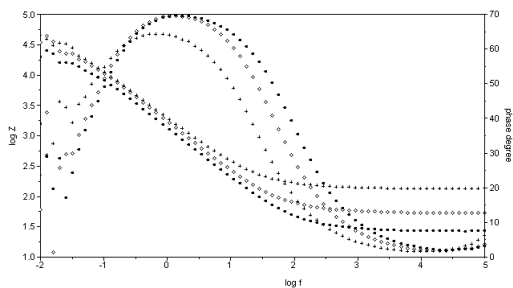


Figure 2. Bode plots for Al electrode at the OCP after 5 minutes of immersion time in aerated aqueous solutions containing, respectively, 20% EG (●), 50% EG (○), 80% EG (+) and 0.1 M L^{-1} sodium borate.

By assuming a parallel plate condenser, the “apparent layer thickness” value, d , for the films formed in several experimental conditions, can be roughly estimated by the expression below:

$$d = (\epsilon \epsilon_0 A) / C$$

where ϵ_0 is $8.85 \cdot 10^{-14} \text{ F cm}^{-1}$, ϵ is the dielectric constant of the surface film, the estimated value of which is 12^3 , A is the exposed area of the electrode and C the overall capacitance obtained from the EIS measurements. The obtained results are given in Table 1. These results indicate the complexity of the interfacial reactions occurring in the system, due to the competitive reactions taking place in the film formation processes. Furthermore, the influence of pH, not yet evaluated, shall be considered in the interpretation of these results.

Table 1: Electrochemical parameters obtained from EIS measurements for the Al electrode.

Solution	20% EG	50% EG	80% EG
$E_{\text{corr}} (\text{V})$	- 1.25	-1.17	- 1.05
$R_s (\Omega \text{cm}^2)$	27	54	137
$R_p (\text{k} \Omega \text{cm}^2)$	23	32	42
$d (\text{\AA})$	14	18	21

CONCLUSIONS

Significant differences were observed in the Al passive behaviour as a function of the solution composition. At the OCP films were formed in EG-water solutions. Under anodic polarization, the breakdown of the passive Al film is favoured by increasing the water content.

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